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Resonant inelastic X-ray scattering at the Be 1s edge in BeO

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Abstract

We present the resonant inelastic X-ray scattering (RIXS) spectra of BeO at the Be 1s photoabsorption edge. The RIXS spectra excited in the vicinity of the core exciton resonance show two principal features: the scattering on a valence exciton (which at higher excitation energies verges into the characteristic Kα emission), and a remarkably strong energy loss side-band to the elastic scattering peak, which has a maximum width of 6 eV and has intensity, at resonance, comparable to the valence scattering. The energy loss side-band appears to result from rapid lattice relaxation at the absorption site on the X-ray scattering time-span.

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Keywords: Resonant inelastic X-ray scattering; X-ray emission; Core exciton

1. Introduction

Insulating oxides have physical properties that make them useful in a wide range of applications. BeO has attracted attention due to its high thermal stability (melting temperature $T_m = 2550\,^{\circ}C$), wide transparency range extending from VUV to IR region (120–7000 nm), high heat conductivity, mechanical hardness and radiation resistance. BeO crystallizes in the hexagonal wurtzite crystal structure, with the lattice point symmetry as low as C_{3V}. A consequence of the low symmetry is the strong anisotropy of the optical constants and luminescence properties.

The RIXS spectroscopy has proven useful for investigations of electronic processes, including the dynamics of core excitations. Unlike photoelectron spectroscopies it is non-sensitive to sample charging, and is particularly useful for crystalline bulk insulator studies for materials, like BeO, which are not easily obtained as thin films without serious stoichiometry issues. A few recent RIXS studies [1,2] are closely related to this present work. Ma et al. [1] observed the long energy loss tail to the elastic scattering peak, while in the absorption spectrum only a relatively sharp core exciton peak was observed. The authors suggested that strong vibronic coupling leads to a local lattice distortion, and to the corresponding shifts in the excited electron state. The appearance of the energy loss side-band in the electronically elastic part of the RIXS spectra indicates that such distortion occurs already during the lifetime of the inner-shell hole. A similar phenomenon is typical of valence excitons in alkali halides and in oxides, where self-trapping of valence excitons occurs in the course of lattice relaxation, and the radiation emitted during the lattice relaxation process has been called "*hot* luminescence". The term *hot luminescence* has even been introduced to describe the processes related to the appearance of the energy loss side-band of the elastic peak in RIXS spectra [2,3]. Recently a similar side-band has been observed in the RIXS spectra of $LiNO_3$ [4], where it was attributed to the dynamics of X-ray emission, accompanying the distortion of NO_3^- species. We present here the RIXS spectra of BeO at Be 1s edge. In these spectra we found extraordinarily strong energy loss side-band to the elastic peak, indicating overwhelming local reconfigurations in the vicinity of the absorption site during the lifetime of the core excitation.

2. Experimental

A BeO crystal of hexagonal prism shape with the natural growth faces was used in this study. The shape of the sample

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allowed easy orientation with respect to the crystal axes. The crystallographic *c*-axis was parallel to the probed sample surface, and the crystal was oriented so that the *c*-axis was perpendicular to both the polarization and the detection directions. The incidence angle was 10° (from the surface normal). The spectrometer (a Gammadata Scienta XES300) was at 90° to the incident beam propagation direction, and parallel to the polarization. The experiments were carried out on beamline I511-3 at MAX-Lab, Lund, Sweden [5]. The resolution of the beamline monochromator (a modified SX700 by Zeiss) was set to 0.1 eV. The resolution of the spectrometer on the end station was set to 0.2 eV. The base pressure of the system was 1×10^{-9} Torr. The measurements were performed at room temperature.

3. Results and discussion

According to the theoretical calculations [6,7], the BeO valence band is split into two distinct bands, separated by an intraband gap. The lower valence band (VB) of BeO is formed by the sp^3-hybridized orbitals of Be and the 2s atomic orbitals of oxygen. The upper VB is composed of a combination of the Be sp^3-hybridized orbitals and the oxygen 2p atomic orbitals, and the conduction band is almost completely composed of the Be 2p atomic orbitals with an insignificant admixture of the oxygen 2p atomic orbitals, whereas the electronic configurations of ions are $Be2s^{0.37}2p^{1.07}$ and $O2s^{1.74}2p^{4.80}$.

Fig. 1 displays the fluorescence yield spectra in the 111–130 eV (the "participator" curve in the figure) and 93–110 eV (the "spectator") detector energy windows. Two strong peaks are seen, at excitation energies 119.3 and 124.6 eV. These main peaks align well with the energy loss spectrum in the *non*-resonant inelastic X-ray scattering (NRIXS) study of BeO of Ref. [8], which also states that the NRIXS spectrum can only be reproduced by calculations if the core hole interaction with the excited electron is taken into account. Their calculations also gave a value of 0.74 eV for the energy distance from the exciton level to the bottom of the conduction band.

The development of the RIXS and several off-resonant X-ray emission spectra at the Be 1s edge of BeO are presented in Fig. 2. The high-energy end of each spectrum is terminated by the sharp elastic scattering peak at incident photon energy. The elastic peak is seen to have an unusually strong energy loss side-band when the excitation is in the proximity of the photoabsorption resonance of 119.3 eV. In the photon energy region 99–109 eV the emission band corresponding to the decay transition from VB to Be 1s level is seen. A very weak X-ray emission band was even observed around 89 eV (omitted from Fig. 2), which reflects the Be contribution to the inner VB.

The low energy cut-off of the low energy tail (LET) of the elastic peak is at nearly constant photon energy, 113 eV, and it extends up to the elastic peak until the excitation energies reach the maximum of the photoabsorption peak at 119.3 eV, thus its maximum width is about 6 eV. When the excitation energy is increased beyond the photoabsorption resonance energy, a valley appears between the LET and the elastic peak and the intensity of the LET quickly decreases. For excitations a few eV above the resonance the LET emission is no longer observable. We

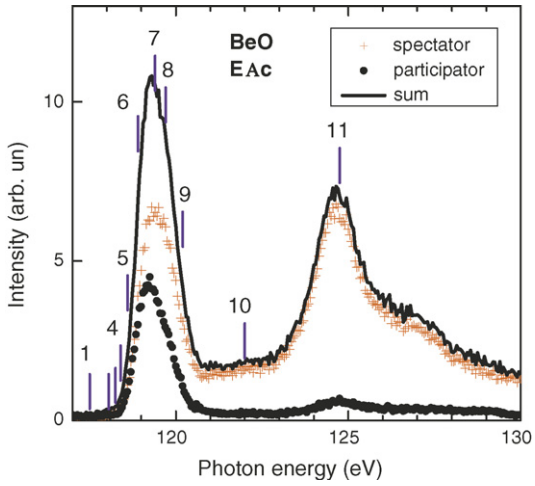

Fig. 1. The Be 1s fluorescence yields of BeO. Crosses and filled circles denote correspondingly the photon yields of the "spectator" (energy window 93–110 eV) and the "participator" (111–130 eV) transitions, measured using the XE spectrometer. Solid line denotes total Be 1s fluorescence yield (the sum of the spectator and the participator yield spectra). The numbered tags denote the excitation energies of the X-ray emission spectra, presented in Fig. 2.

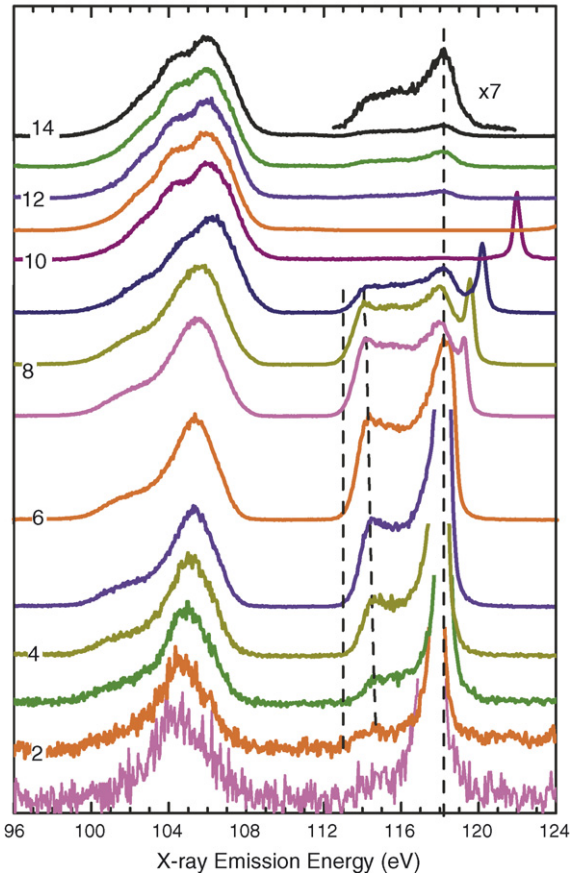

Fig. 2. The Be 1s RIXS spectra of BeO. The numbers denote incident photon energies as marked in Fig. 1. Excitation energies for the off-resonant X-ray emission spectra 12, 13 and 14 are 131, 133 and 145 eV, correspondingly.

suggest that the LET band to the elastic peak appears due to the dynamic lattice distortion at the absorption site on the X-ray emission time-scale, in line with the arguments in Refs. [2,4]. When the excitation energy is increased even further and reaches values of approximately 130 eV, a satellite band, similar to the LET, appears again to the off-resonant X-ray emission spectra, although its intensity then is substantially weaker. This energy, 130 eV, coincides well with the sum of band gap (10.6 eV) and photoabsorption maximum (119.3 eV). Such second threshold indicates that the band, which we observe as the LET in the case of resonant excitation, can be excited when the energy of valence photoelectron reaches the energy of core exciton [9].

We call the emission above the valence band top emission energies (the elastic peak and the LET) the *participator* emission (the excited electron participates in the decay event, i.e., the emission is due to the transition of the excited electron to the 1s level). The area of the sharp elastic scattering peak measures the transition without relaxation and the area of LET is a measure of the transition with the relaxation. At resonance, the small area of the sharp elastic peak in comparison to the LET shows that at photoabsorption resonance in most cases the relaxation has started. However, we would like to mention here, that the intensity ratio between LET of the elastic peak and the spectator emission is constant for fixed excitation energy, but the relative intensity of sharp elastic peak changed strongly when we changed position at the crystal surface. This shows that the elastic scattering at the surface (reflection) gives its contribution to the sharp elastic scattering peak, but the intensities of the inelastic processes (the spectator and the LET participator band) reflect the fundamental properties of the bulk crystal. It should be at the same time kept in mind that the elastic peaks is weaker, but does not vanish elsewhere. The participator emission is, however, the only possible channel for the LET emission, because there are no other electrons available for this transition.

We now draw attention to the observation, that the LET of the elastic peak has two maxima—at approximately 114.7 and 118.4 eV. Note that the lower energy maximum (114.7 eV) shifts slightly (less than 0.5 eV) to lower emission energies when the excitation energy exceeds the photoabsorption resonance. The higher energy maximum at 118.4 eV has emission energy which is about 1 eV lower than the energy of photoabsorption resonance.

The participator transitions in solids can be treated as Frank-Condon transitions in systems of two potential curves, presented as a function of internuclear distance for molecules, or as a function of the configuration coordinate in solids. However, if the neighborhood of the excited atom becomes considerably altered during the core excited state lifetime, it becomes meaningful to introduce a third potential curve (see Fig. 3), which can be shifted in equilibrium coordinate and elasticity parameters. Earlier, Ma et al. [1] have emphasized the similarity between the core exciton in carbon and the self-trapped excitons (STE) in alkali halides [1] as they both relax to an off-center configuration upon generation. Soon after that it has been shown for carbon, that the reason for the appearance of a LET is the self-trapping of core exciton [10]. If we now suppose that even the

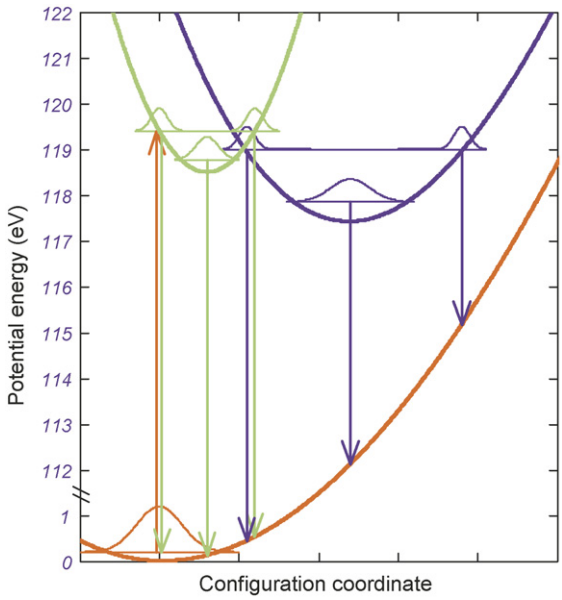

Fig. 3. Schemes of possible transitions in the RIXS participator channel. The bottom curve: ground electronic state; the curve at top left: unperturbed unoccupied state potential; the curve at top right: excited state potential modified by local lattice relaxation. See text for further details.

Be 1s exciton in BeO becomes, similarly, self-trapped then the whole process should be described in the following manner—the photoabsorption makes the transition of an electron from the ground state to the intermediate state (the top left curve in Fig. 3); however lattice distortion will change the potential curve so that the decay already occurs from a relaxed state (top right curve in Fig. 3). The relaxation processes also cause the system to "slide down" along the excited state potential curves, and if the relaxation rate is comparable to that of the decay processes, this leads to the emission from different states on the potential curves of the excited state. If the relaxation is very fast, the system promptly relaxes to the minimum of excited state curve, and only the transition from the minimum should be seen (indicated by the second arrow from the right). The observed wide LET shows that the transitions are from a progression of intermediate states in different stages of relaxation, which makes the whole process similar to the hot luminescence in the optical region.

It is interesting to note that in the excitation spectra of the spectator band the two peaks are of almost equal intensity (similarly to the energy loss spectrum of NRIXS in BeO [8]), but in the participator band excitation spectrum the 124 eV maximum is almost absent, indicating the absence of core excitons at this excitation energy. Even the first excitation resonance can be divided into two energy regions: below the participator peak maximum (at 119.2 eV) a strong side-band appears in RIXS to the elastic peak, indicating strong localization of the excited electron. Above this energy, the participator band looses its intensity faster than the spectator band, and the spectator channel (with maximum at 119.4 eV) starts to dominate. The weakening of the participator band suggests increasing delocalization probability for the excited electron. As stated above, the appearance of the broad participator emission indicates strong localization

of the excited electron, therefore we consider the participator excitation spectrum as predominantly the core exciton excitation curve.

The spectator band emission is known in the case of off-resonant excitation as Be Kα X-ray fluorescence and it is commonly assumed that due to the dipole selection rules it reflects the density of p-states at the Be ion. In the case of resonant excitation this emission band can be described as the "spectator" emission, because the excited electron acts as a spectator during the core hole decay process. Increasing the excitation energy in the absorption resonance region makes the spectator band maximum to shift to higher photon energies, which reflects the RIXS energy conservation. In the case of resonant excitation the maximum of this band is at about 1 eV lower photon energy as compared to the off-resonant excitations. A similar shift has been observed earlier for spectator transitions in many cases. It reflects the phenomenon that the ionization energy for the spectator electron is usually larger in the core excited state than in the valence excited state (Ref. [4] and references therein). The spectator shows additional structures at off-resonant excitation (spectra 12–14 in Fig. 2).

Above we described the participator emission as strongly influenced by the lattice relaxation. We speculate, that even the Be 1s spectator emission should be sensitive to the relaxations. This is supported by a recent study on adsorbed ethylene [11], where it is shown by the comparison of calculated and measured spectra. Similarly to the case of radiative participator decay, this may lead to the widening of the corresponding VB spectra in comparison with the calculated VB density of states [6,7]. Considering this, we may interpret the changes in the spectator spectrum as indications of analogous energy loss features. However, due to the overlap of different final states these effects not be as clearly distinguished as in the case of participator band.

4. Conclusions

We have observed a 6 eV wide and very intense energy loss side-band to the elastic X-ray scattering peak at the Be 1s edge in BeO. We propose that this spectral feature originates in a local lattice rearrangement to an energetically more favorable configuration around the introduced core hole, and that the whole process is mediated by large vibronic coupling to vibrations about the shifting equilibrium coordinates. Further, we emphasize that the relaxation process in BeO can be considered fast even on the time-scale of soft X-ray scattering, since the broad RIXS spectra containing no sharper features except a sharp low energy cut-off indicates that the RIXS events occur at all stages of the relaxation process.

Acknowledgments

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